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<p>(54) Title: SUPPORTED BF₃-COMPLEX SOLID ACID CATALYST, PREPARATION AND USE</p>		
<p>(57) Abstract</p> <p>A novel method to prepare solid acid catalysts by the reaction of liquid BF₃ precursors with inorganic oxide supports is reported. The resulting solid acid catalyst exhibits strong Brønsted acidity that can be tuned by appropriate selection of cocatalyst, solvent or calcination temperature, and can be used to catalyse organic reactions.</p>		

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Supported BF₃-complex solid acid catalyst, preparation and use**Background to the invention:**

Tightening environmental legislation on the production of waste during homogeneously acid catalysed reactions has led to a demand for heterogenised systems that will aid recovery of the catalyst and minimise pollution. Conventional Lewis acids (e.g. AlCl₃ and BF₃) catalysts are used extensively in a range of industrial processes, including alkylation, acylation, polymerisation, isomerisation and addition reactions. The major drawback of these catalysts stems from the need to purify the product to remove catalyst residues and the need to dispose of large volumes of contaminated waste produced during separation of the catalyst from the product/reactant mix. The activity of these catalysts is also difficult to control and in many systems they produce undesirable biproducts thus reducing reaction yield.

Solid acid catalysts suitable for the alkylation of isobutane with butenes have been proposed in Applied Catalysis A: General 107 (1994) 239 to 248. These catalysts consist of H₃PO₄-BF₃-H₂SO₄ supported on SiO₂ and ZrO₂. These catalysts however suffer from the disadvantage that they contain undesirable materials particularly phosphorous, they involve the use of mineral acids which are corrosive and they are proposed for use only in gas phase systems. Further the method of preparation uses the phosphoric acid to act as a bridge between the surface of the support and the BF₃ and the presence of water and sulphuric acid as well as the heating to dry the catalyst leaves doubts as to the nature of the catalytic species.

This invention specifically concerns the preparation of supported BF₃ catalysts for use in liquid organic reactions. The use of a heterogeneous catalyst in these reactions would offer ease of separation and catalyst recycling, and thus reduce the waste effluent currently produced which is essential if the chemical industry is to comply with ever tightening environmental legislation on the production of waste. However a suitable replacement supported system must also exhibit activities/selectivity's comparable to or superior to the existing homogeneous route.

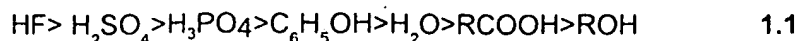
A method for supporting AlCl₃ on SiO₂ has been previously reported in US Patent 5 294 578 which involves the reaction of Al-Cl bonds with hydroxyl groups on SiO₂ to form Al-O-Si bonds liberating HCl in the process. Previous attempts to support BF₃ have been reported using Al₂O₃ (US Patent 4 407731

and WO 94/02243) or zeolites (US Patent 4 709110) as the support material but have required the use of gaseous BF_3 . The BF_3 sites formed on Al_2O_3 are reported as being only partially supported when used in liquid reactions. Often solvents such as diethyl ether are used to make a slurry with the support material, gaseous BF_3 is then bubbled through the slurry. This can result in the formation of BF_3OEt_2 complexes which are known to be catalytically active in polymerisation reactions. There are however no reported patents or literature that involve the use of a liquid precursor to attach BF_3 -cocatalyst complexes to the surface of inorganic oxide supports.

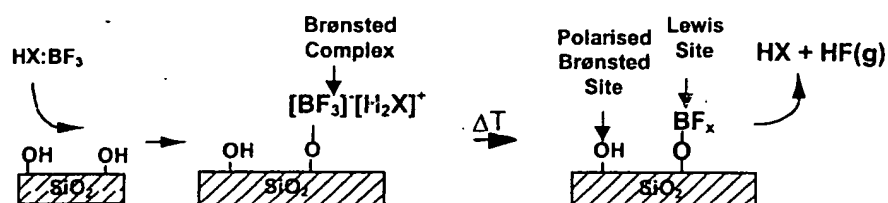
The present invention provides a new supported BF_3 catalyst system in which BF_3 is attached directly to the surface of the support and which incorporates an organic cocatalyst to control acidity and catalytic activity. The novel form of supported BF_3 /cocatalyst complex exhibits Brønsted and Lewis acid properties that can be tuned by varying both the cocatalyst and the catalyst preparation techniques. Unlike the oxide supported solid acid catalysts described in earlier work which involve the use of gaseous BF_3 in their preparation, our route enables liquid BF_3 complexes to be supported directly on the support (preferably silica) surface. This simplifies the preparation, and also enables the loading of BF_3 to be tuned more precisely. BF_3 precursors are known to be unstable towards hydrolysis liberating HF. However, when attached to the support the hydrostability of the precursor is strongly dependent on the preparation route used.

The present invention therefore provides a supported BF_3 catalyst system comprising a BF_3 /organic Brønsted base cocatalyst complex wherein BF_3 is attached directly to the surface of the support.

The catalytic activity of homogeneous BF_3 complexes in many organic reactions is dependent on the ability of the complex $[\text{H}^+][\text{X}:\text{BF}_3^-]$ to act as a proton donor to olefins. The activity of the cocatalyst (HX) in homogeneous systems is observed to decrease in the order (see GA Olah "Friedel Crafts and Related Reactions", Volume 2, Interscience Publishers, 1940).



By supporting different polarisable proton donating BF_3 complexes on supports such as SiO_2 , the tuneable catalytic activity observed in the homogenous system should be obtained with the advantage of ease of catalyst recovery of a heterogeneous solid acid. Subsequent thermal treatment of the catalyst should also enable additional tuning of the relative amounts of Lewis and Brønsted acid sites present, as summarised below.



Brønsted acidity in solid acid catalysts normally arises from polarised $-\text{O}-\text{H}^+$ sites. The observation of strong Brønsted acidity following attachment of a Lewis acid centre to an oxide support has been reported in other systems, and is attributed to polarisation of surface hydroxyl groups *via* an inductive effect of the electronegative halogen atoms on the acid site. In our model, additional Brønsted acidity is obtained from the Brønsted complex illustrated above. We have found that it is important that once formed the supported catalyst system should not be unduly heated since this can result in the loss of the cocatalyst. Low temperatures should therefore be used in catalyst preparation, care must be taken in any drying of the catalyst and calcination is preferably avoided.

By varying the complexing ligand HX , the Brønsted complex acidity can be varied. The organic Brønsted base is an organic molecule containing oxygen, nitrogen or sulphur basic centres capable of being protonated to produce the desired catalyst acidity typically a Pka value of +4 or lower, preferably -1 or lower. Preferred are those organic molecules containing an oxygen basic centre such as alcohols, ethers, ketones, aldehydes, ethoxylates, carboxylic acids or mixtures thereof. Particularly preferred are alcohols and carboxylic acids. Water may also be used in admixture with such organic molecules. The choice of solvent (which can also complex with the BF_3) used during the preparation will alter the acidic properties of the catalyst. The catalyst systems of this invention are usually produced by mixing the BF_3 /Brønsted complex with the support in a solution. The solvent can therefore be chosen according to the acidic properties required in the catalyst system for example polar solvents

(alcohols) will result in enhanced Brønsted acidity compared to nonpolar solvents (such as aromatic hydrocarbons). It is preferred that the solvent used in the preparation is predried to avoid hydrolysis of the BF_3 complex.

Characterisation of these solid acids by MAS-NMR, DRIFTS and pyridine titration enable the Brønsted or Lewis acid characteristics of the different catalysts to be determined. We also expect that the thermal stability of these complexes will vary depending on the precursor used. Thus the relative amount of Brønsted:Lewis acid sites can be tuned by precalcining the samples under an inert atmosphere.

The catalyst when used in reactions can be recovered by filtration and reused in subsequent reactions.

The nature of the support used in the catalyst system of the present invention is also important. It must be able to react with the BF_3 and can be chosen according to the nature of the reaction to be catalysed and the cocatalyst. Examples of suitable supports are materials containing surface hydroxyl groups such as silica synthetic silicas (MCM) hexagonal mesoporous silica (HMS) as described in Nature 1992 359, page 710 and Science 267 page 865, and clay supports, including naturally occurring clay mineral such as kaolinite, bentonite, attapulgite, montmorillonite, clarit, Fuller's earth, hectorite, and beidellite; synthetic clay such as saponite and hydrotalcite; montmorillonite clay treated with sulphuric acid and/or hydrochloric acid; and modified clay such as Aluminium oxide pillared clay, cerium modified alumina pillared clay, and metal oxide pillared clay. The preferred supports have surface hydroxyl groups which can react with the Boron trifluoride, mesoporous silica and silica calcined at 500°C or above, preferably 600°C and above are particularly preferred support.

The support may also include at least one member selected from the group consisting of zeolite β , zeolite Y, zeolite X, MFI, MEL, NaX, NaY, faujasite, mordenite, alumina, zirconia, titania and alumino silicates.

The catalyst systems of the present invention may be used in the wide variety of reactions where acid catalysts have been traditionally used. The use of the catalysts brings the benefits of cleaner reaction (less product purification required, less waste disposal problems) and the ability to tune the catalyst to the reaction so increasing yields and specificity. Examples of reactions in which the catalysts may be used include alkylation, polymerisation,

etherification, esterification and condensation reactions. We have found that the use of the catalyst systems of this invention in the alkylation of aromatics gives greater control over the position and number of alkylations on the aromatic nucleus.

The yield of the reactions are dependent on the accessibility of the reactants to the catalytic sites. Accordingly the reaction conditions should be adjusted according to the differing characteristics of the substrates. For example, we have found that in the alkylation of aromatics if the alkylating alkene is present in excess of the aromatic the yield is considerably reduced. We prefer therefore to operate under conditions in which the alkene is added gradually in a way which maintains a molar excess of the aromatic. Furthermore, in certain condensation reactions which can produce molecules capable of further condensation the conditions can be tailored to increase the yield of the first or second reaction products. An example is the condensation of 2-hydroxy acetophenone with benzaldehyde to 2¹ hydroxychalcone and the subsequent ring condensation of the 2- Hydroxychalcone to flavanone.

The catalysts of the present invention can therefore be used in the production of a wide range of useful chemicals and chemical intermediates.

The present illustration is illustrated by the following examples:

EXAMPLE 1

A series of catalysts were prepared using different cocatalysts and solvents.

CATALYST A: $BF_3(H_2O)_2/SiO_2$ prepared in ethanol

40 mmol $BF_3(H_2O)_2$ was added to a three necked flask purged with N_2 , containing 100ml of absolute ethanol. 10 g of SiO_2 (K100 - predried at 300°C) was then added and the slurry stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess EtOH was removed under vacuum at 50°C.

CATALYST B: $BF_3(H_2O)_2/SiO_2$ prepared in toluene

40 mmol $\text{BF}_3(\text{H}_2\text{O})_2$ was added to a three necked flask purged with N_2 , containing 100ml of anhydrous toluene. 10 g of SiO_2 (K100 - predried at 300°C) was then added and the slurry stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess toluene was removed under vacuum at 50°C .

CATALYST C: $\text{BF}_3\cdot\text{OEt}_2/\text{SiO}_2$ prepared in ethanol

40 mmol $\text{BF}_3\cdot\text{OEt}_2$ was added to a three necked flask purged with N_2 , containing 100ml of absolute ethanol. 10 g of SiO_2 (K100 - predried at 300°C) was then added and the slurry stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess EtOH was removed under vacuum at 50°C .

CATALYST D: $\text{BF}_3\cdot\text{OEt}_2/\text{SiO}_2$ prepared in toluene

40 mmol $\text{BF}_3\cdot\text{OEt}_2$ was added to a three necked flask containing purged with N_2 , containing 100ml of anhydrous toluene. 10 g of SiO_2 (K100 - predried at 300°C) was then added and the slurry stirred under reflux for 2 hours. The slurry was then transferred to the rotary evaporator where the excess toluene was removed under vacuum at 50°C .

CATALYST E: $\text{BF}_3(\text{CH}_3\text{COOH})/\text{SiO}_2$ prepared in ethanol

40 mmol $\text{BF}_3(\text{CH}_3\text{COOH})$ was added to a three necked flask purged with N_2 , containing 100ml of absolute ethanol. 10 g of SiO_2 (K100 - predried at 300°C) was then added and the slurry stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess EtOH was removed under vacuum at 50°C .

CATALYST F: $\text{BF}_3(\text{MeOH})/\text{SiO}_2$ prepared in methanol

40 mmol $\text{BF}_3\cdot\text{MeOH}$ was added to a three necked flask purged with N_2 , containing 100ml of methanol. 10 g of SiO_2 (K100 - predried at 300°C) was then added and the slurry stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess methanol was removed under vacuum at 50°C .

CATALYST G: $\text{BF}_3\cdot\text{OEt}_2/\text{SiO}_2$ prepared in diethyl ether

40 mmol $\text{BF}_3\cdot\text{OEt}_2$ was added to a three necked flask purged with N_2 , containing 100ml of diethyl ether. 10 g of SiO_2 (K100 - predried at 300°C) was then added and the slurry stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess ether was removed under vacuum at 50°C .

CATALYST H: $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ prepared in ethanol (SiO_2 precalcined 600°C)

40 mmol $\text{BF}_3(\text{H}_2\text{O})_2$ was added to a three necked flask purged with N_2 , containing 100ml of absolute ethanol. 10 g of SiO_2 (K100 - predried at 600°C) was then added and the slurry stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess EtOH was removed under vacuum at 50°C .

CATALYST I: $\text{BF}_3(\text{H}_2\text{O})_2/\text{HMS}_{24}$ prepared in ethanol

40 mmol $\text{BF}_3(\text{H}_2\text{O})_2$ was added to a three necked flask purged with N_2 , containing 100ml of absolute ethanol. 10 g of HMS_{24} (SA $1100\text{m}^2\text{g}^{-1}$) was then added and the slurry stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess EtOH was removed under vacuum at 50°C .

**Preparation of HMS_{24}*

HMS₂₄ was prepared according to the sol gel route of Pinnavaia *et al* by condensing 62.5g of tetraorthoethoxysilicate in a mixture of 123g ethanol and 160g H₂O with 15.3g n-dodecylamine as the surfactant template. The resulting gel was stirred for 24 hours, filtered, dried and then calcined at 600°C for 6 hours to remove the template.

CATALYST J: BF₃.OEt₂/SiO₂ prepared in toluene at 30 °C

40 mmol BF₃.OEt₂ was added to a three necked flask purged with N₂, containing 100ml of anhydrous toluene. 10 g of SiO₂ (K100 - predried at 300°C) was then added and the slurry and was stirred at 30°C for 2 hours. The slurry was then transferred to the rotary evaporator where the excess toluene was removed under vacuum at 50°C.

EXAMPLE 2

Characterisation of Acid sites

Pyridine titration

- (a) Characterisation of the supported BF₃/SiO₂ catalysts was performed using DRIFTS in conjunction with pyridine titration which show that the catalysts A to C exhibit both Lewis and Brønsted acidity (**Figure 1**). This is determined by the absorption bands observed in DRIFT spectra at 1445 and 1461 cm⁻¹, (Lewis sites), 1638 and 1539 cm⁻¹ (Brønsted sites) and 1611 and 1489 cm⁻¹ (combined Lewis/Brønsted sites). There is a striking difference in the nature of the acid sites depending on catalyst preparation, with the catalysts prepared in ethanol exhibiting higher concentrations of Brønsted acid sites than those prepared in toluene. The lack of absorption at 1540 for catalyst D is believed to be due to either the use of reflux conditions in its preparation driving off the cocatalyst or that toluene is insufficiently polar to encourage bond polarisation.

- (b) The corresponding DRIFTS/pyridine titrations of catalysts calcined to 200 and 400°C under Nitrogen, (shown in **Figure 2**) indicate that the

Brønsted sites are gradually lost as the calcination temperature is increased. The most dramatic decrease in Brønsted acidity occurs once ethanol desorption is complete.

A comparison of a range of catalysts prepared using different BF_3 complex precursors is shown in Figure 3. The Brønsted acidity of the catalysts can be determined by pyridine titration. The peak observed at 1540 cm^{-1} is a unique vibrational mode of the pyridinium ion that forms via interaction of pyridine with Brønsted sites. Thus the intensity of this peak provides an indication of presence of Brønsted acid sites on the solid catalyst. Thus it can be seen that if $\text{BF}_3\cdot\text{OEt}_2/\text{SiO}_2$ is prepared in toluene at either reflux or 30°C (Catalyst D and J) the Brønsted acidity is negligible. This is most likely due to a combination of decomposition of the etherate complex and low solvent polarity discouraging bond polarisation.

If however $\text{BF}_3\cdot\text{OEt}_2/\text{SiO}_2$ is prepared in OEt_2 at 30°C , then Brønsted sites are detected due to the formation of $[\text{OBF}_3][\text{Et-OH}^+-\text{Et}]$ complex. Likewise for the other BF_3 precursors tested a high degree of Brønsted acid character persists due to the presence of protic complexes. It should be noted however that these titrations simply indicate the presence of Brønsted sites, but are not related to the Brønsted acid strength.

TGIR

(b) The origin of the acid sites on the ethanol prepared catalysts A and C was investigated using thermogravimetric analysis coupled with evolved gas FTIR (TGIR), which allows molecules desorbing from the catalyst during thermal analysis to be identified by their vibrational spectrum. Heating both catalysts above 100°C results in significant weight loss and the observation of ethanol desorption in the IR. However the differential mass lost indicates that the ethanol desorption temperature from $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ is 10°C higher than from $\text{BF}_3\cdot\text{OEt}_2/\text{SiO}_2$, and approximately twice the amount of ethanol is evolved. The uptake of short chain alcohols can be used as an indication of the strength and concentration of Brønsted acid sites on zeolites. These

results therefore suggest that $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ possesses a higher coverage of stronger Brønsted acid sites compared to $\text{BF}_3\cdot\text{OEt}_2/\text{SiO}_2$. Further heating beyond 400°C results in an additional weight loss which is accompanied by the evolution of HF from the catalyst.

MAS-NMR

The evolution of ethanol above 100°C coupled with the loss of Brønsted acidity indicates that Brønsted acid sites in the $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ catalyst may arise from the binding of ethanol to supported BF_3 centres resulting in the formation of a $[\text{SiOBF}_3]^-[\text{EtOH}_2]^+$ complex.

Further evidence in support of this model comes from ^1H MAS NMR of the as prepared catalyst which show resonances at 1.34, 4.01 and 8.16 ppm which are consistent with CH_3 , CH_2 and OH_2^+ of protonated ethanol respectively.

BET Surface Area:

Sample	Surface Area m^2g^{-1}
K100 SiO_2	300
Catalyst A as prepared	259
Calcined 150°C	258
Calcined 400°C	267
Calcined 600°C	56

Loss of surface area on calcining at 600°C is ascribed to formation of a borosilicate species.

EXAMPLE 3

Phenol Alkylation by 1-octene –using solvent

(a) The catalytic activity of various supported BF_3 samples was tested using the reaction of 1-octene with phenol (performed at 85°C using 0.05 M of each reactant, in 100 ml of 1,2 dichloroethane with 1g of supported BF_3 catalyst). **Table 1** shows the phenol conversion and selectivities towards octyl-phenyl ether obtained after 23 hours reaction time. It is clear that the activity of the $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ catalyst prepared in ethanol is superior to the other samples. The activity can thus be correlated with the number and strength of Brønsted acid sites identified on these catalysts using TGIR.

(b) Following reuse of $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ samples, a decrease in conversion and selectivity towards ring alkylation products is observed relative to the fresh catalyst. The loss of activity on recycling the catalyst may result from organic residue deposited on the catalyst during reaction causing pore blocking and/or poisoning of active sites.

Catalyst	Phenol Conversion (%)	Ether Selectivity (%)
A $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ (EtOH)	30	61
A $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ - recycled	6	97
B $\text{BF}_3(\text{H}_2\text{O})_2/\text{SiO}_2$ (PhCH ₃)	4	78
C $\text{BF}_3(\text{OEt}_2)/\text{SiO}_2$ (EtOH)	3	85
D $\text{BF}_3(\text{OEt}_2)/\text{SiO}_2$ (PhCH ₃)	<1	92

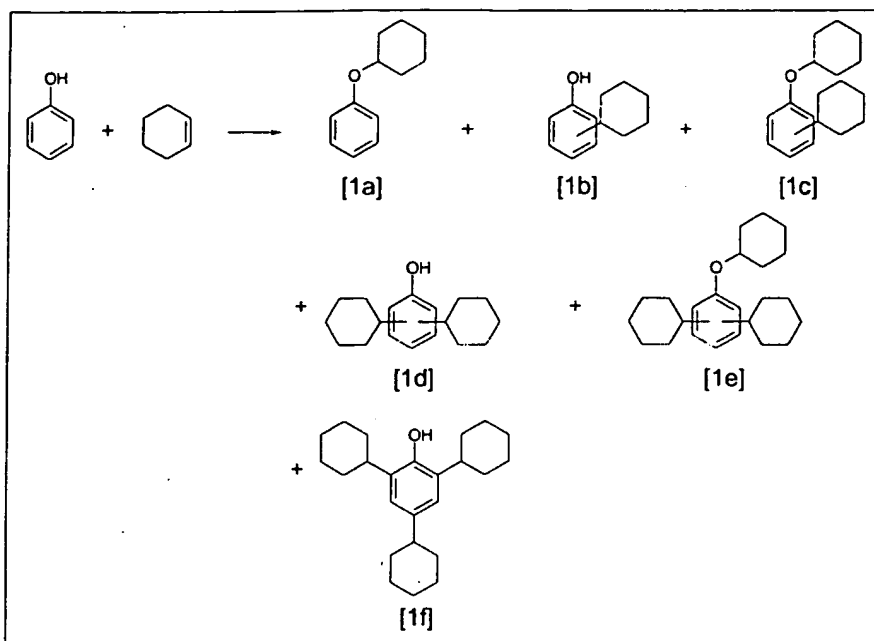
Table 1

EXAMPLE 4

Phenol Alkylation by cyclohexene – Optimisation of Reaction Conditions

A problem of using linear alkenes in alkylation reactions, is that they readily isomerise resulting in a wide range of alkylation products. To simplify the

reaction conditions and assist with optimisation of performance of Catalyst A, cyclohexene was selected as the alkene as isomerisation will not occur. The range of products expected are shown in scheme 1.



Scheme 1

Five cases are compared

- I. 2.3g of phenol, 2.0 g of cyclohexene, 1.0g of dodecane (internal standard) and 25 ml 1,2 Dichloroethane was added to a three necked round bottomed flask and heated to 85°C. 0.6g of supported catalyst A was then added to the reaction and samples taken periodically for analysis by GC.
- II. 2.3g of phenol, 1.0g of dodecane (internal standard) and 25 ml of 1,2 Dichloroethane was added to a three necked round bottomed flask and heated to 85°C. 0.6g of supported catalyst was then added to the reaction then 2.0g of cyclohexene was added gradually using a peristaltic pump. Samples were taken periodically from the reaction for analysis by GC.

- III. 2.3g of phenol, 2.0 g of cyclohexene and 1.0g of dodecane (internal standard) was added to a three necked round bottomed flask and heated to 85°C. 0.6g of supported catalyst A was then added to the reaction and samples taken periodically for analysis by GC.
- IV. 2.3g of phenol, and 1.0g of dodecane (internal standard) was added to a three necked round bottomed flask and heated to 85°C. 0.6g of supported catalyst was then added to the reaction then 2.0g of cyclohexene was added gradually using a peristaltic pump. Samples were taken periodically from the reaction for analysis by GC.
- V. 2.3 g of Phenol, 6.0g cyclohexene and 1.0g of dodecane (internal standard) was added to a three necked round bottomed flask and heated to 85°C. 0.6g of supported catalyst A was then added to the reaction and samples taken periodically for analysis by GC.

The results of these tests are shown in **Figure 4**, which illustrates that the conversion of phenol decreases from experiment

$$IV > III > II > I$$

Thus phenol conversion can be increased if the alkene is added gradually over the period of the reaction.

No Phenol conversion was observed with reaction V, illustrating that phenol alkylation is diffusion limited, and that excess alkene poisons the reaction, presumably due to the formation of oligomers at the active site.

¹⁹F NMR showed no detectable fluorine compounds present in the reaction mixture after filtration.

Example 5

Comparison of Catalyst Performance

a. Effect of precursor/cocatalyst

2.3g of phenol, 2.0 g of cyclohexene and 1.0g of dodecane (internal standard) was added to a three necked round bottomed flask and heated to 85°C. 0.6g of supported catalyst was then added to the reaction and samples taken periodically for analysis by GC. The product distribution obtained after 8 hours reaction time using 3 catalysts A, E, and G are compared in **Figure 5**.

Ring alkylation requires stronger acid sites. From **Figure 5** it can be seen that catalyst G results in higher conversions of Phenol, and higher selectivity towards ring alkylated products. These observations are consistent with the respective pKa's of the cocatalyst EtOH⁺Et and EtOH₂⁺ listed in table 2 . The exact nature of the cocatalyst formed with catalyst E is uncertain. Possible Bronsted acid species include CH₃COOH₂⁺, CH₃C(OH⁺)OEt, EtOH₂⁺, and CH₃COOH. As the catalyst was prepared in EtOH, the EtOH₂⁺ complex may dominate .

Complexing Ligand	pKa
H ₃ O ⁺	-1.7
MeOH ₂ ⁺	-2.0
C ₂ H ₅ OH ₂ ⁺	-2.4
$\begin{array}{c} \text{R}-\text{O}^+-\text{R} \\ \\ \text{H} \end{array}$	-3.5
CH ₃ COOH ₂ ⁺	-6.0
CH ₃ C(OH ⁺)OEt	-6.5

Table 2

b. Effect of support material

The effect of precalcination temperature of K100 SiO₂, and the use of mesoporous silica HMS₂₄ is compared using the BF₃(H₂O)₂ precursor in EtOH.

2.3g of phenol, 2.0 g of cyclohexene and 1.0g of dodecane (internal standard) was added to a three necked round bottomed flask and heated to 85°C. 0.6g of supported catalyst was then added to the reaction and samples taken periodically for analysis by GC. The product distribution obtained after 8 hours reaction time using 3 catalysts A, H and I (all prepared using $\text{BF}_3(\text{H}_2\text{O})_2$ precursor in EtOH) are compared in **Figure 6**.

Catalysts H and I, prepared using 600°C calcined SiO_2 and HMS_{24} materials respectively as the support are slightly more active for phenol alkylation than catalyst A. Catalysts H and I also exhibit higher selectivities towards ring alkylated products compared to the analogous catalyst prepared on K100 SiO_2 (catalyst A). These results may be ascribed to 600°C calcined K100 and HMS_{24} having different surface polarities compared to conventional silica. This physical property will alter the diffusion rates of the reactants/products and in turn alter product selectivities. Another beneficial effect of high temperature calcination of silica, is that the surface becomes more hydrophobic, which will increase the stability of BF_3 sites towards hydrolysis.

c. Effect of Solvent used in catalyst preparation

Catalyst G (prepared from BF_3OEt_2 in OEt_2) exhibits the highest activity in phenol alkylation. In contrast Catalyst D (prepared from BF_3OEt_2 in refluxing PhMe) exhibits very low activity. To understand whether this is due to toluene being a poor solvent for catalyst preparation, or if refluxing is impairing catalyst acidity, catalyst J was prepared in toluene at 30°C as a control.

2.3g of phenol, 2.0 g of cyclohexene and 1.0g of dodecane (internal standard) was added to a three necked round bottomed flask and heated to 85°C. 0.6g of supported catalyst was then added to the reaction and samples taken periodically for analysis by GC. The product distribution obtained after 8 hours reaction time using 3 catalysts D, G and J are compared in **Figure 7**.

Both catalysts D and J exhibit low phenol conversions, suggesting that reduced catalyst activity originates from using toluene as a solvent during catalyst preparation. Under these conditions, the most active catalyst results from using diethyl ether during catalyst preparation.

EXAMPLE 6

Effect of calcination on catalyst activity:

A sample of catalyst A was calcined at 150°C under Nitrogen for 2 hours.

2.3g of phenol, 2.0 g of cyclohexene and 1.0g of dodecane (internal standard) was added to a three necked round bottomed flask and heated to 85°C, then 0.6g of calcined catalyst was added to the reaction and samples taken periodically for analysis by GC. The results of this experiment after 24 hours reaction are compared with those for the uncalcined catalyst in Table 3.

Catalyst	PhOH Conversion%	Ring alkylation selectivity%
Catalyst A calcined 150°C	6	10
Catalyst A as prepared	38	30

Table 3

Following calcination the activity of the catalyst is considerably reduced, and the selectivity ring alkylated products decreases. This can be understood in terms of the loss of EtOH_2^+ complex and reduced Brønsted acid strength of the calcined catalyst.

EXAMPLE 7

Comparison with homogeneous $\text{BF}_3(\text{H}_2\text{O})_2$:

2.3g of phenol, 2.0 g of cyclohexene and 1.0g of dodecane (internal standard) was added to a three necked round bottomed flask and heated to 85°C, then 0.3g of $\text{BF}_3(\text{H}_2\text{O})_2$ was added to the reaction and samples taken periodically for analysis by GC. The results of this experiment are shown in **Figure 8** and may be compared with those for the Catalyst A.

A comparison of phenol alkylation using the homogeneous and heterogenous versions of the $\text{BF}_3(\text{H}_2\text{O})_2$ precursor is shown in **Figures 8 and 9**, from which it can be seen that the product distributions obtained are quite different. The heterogeneous catalyst forms ether products with a high selectivity that is maintained throughout the reaction. However for the homogeneously catalysed reaction the ether selectivity reaches a maximum, then decreases as the reaction proceeds with a concomitant increase in the yield of ring alkylated products.

These results can be interpreted in view of observations that unlike homogeneous $\text{BF}_3(\text{H}_2\text{O})_2$, $\text{BF}_3(\text{H}_2\text{O})_2/\text{EtOH}/\text{SiO}_2$ does not rearrange cyclohexyl-phenyl ether. However, ether rearrangement by the homogeneous system results in the formation of phenol and dialkylated products, suggesting that the rearrangement involves cracking of the C-O bond yielding a cyclohexyl cation which can subsequently perform ring alkylation reactions.

EXAMPLE 8

Polymerisation of methyl styrene

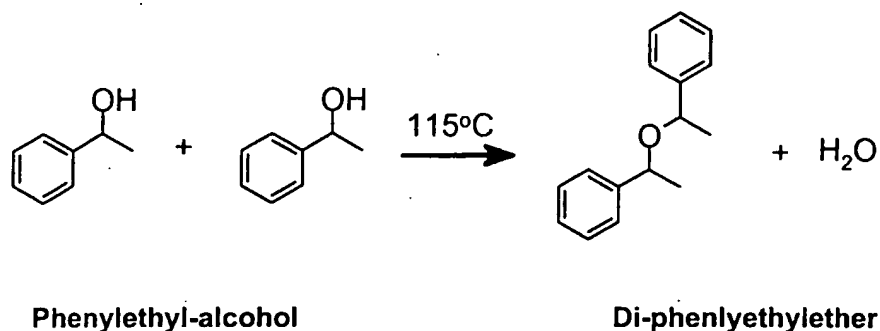
20 ml of 4-methyl styrene was added to a flask containing 20 ml of anhydrous toluene. 0.2 g of Catalyst A was added and the reaction stirred for 1.5 hours at 20°C. The reaction was terminated by filtering off the catalyst. The light fractions were removed by stripping under vacuum, leaving a viscous white

solid. The overall yield of polymer based on the original mass of monomer was 26%.

EXAMPLE 9

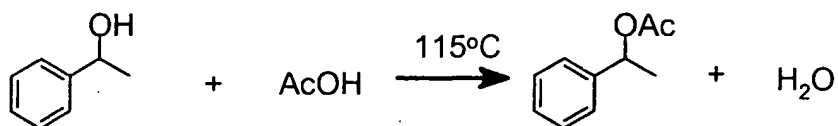
Etherification

7.0g of sec-phenylethyl alcohol was stirred at 120°C with 1.0g of catalyst A. After 2 hours the reaction was analysed by GC, which indicated that 72% of the alcohol was converted to diphenyl ether with a selectivity of 100%.



EXAMPLE 10

Esterification Reactions



Phenylethyl-alcohol Acetic Acid

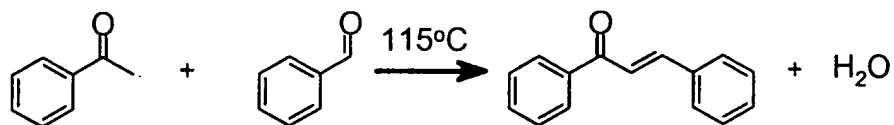
3.6 g of Phenethyl alcohol was added to 5g of acetic acid with 0.5g of dodecane as internal standard. The mixture was heated to 120°C, then 1g of catalyst A added. Analysis of the reaction after 2 hours revealed 80% of the alcohol had reacted. The selectivities were as follows

acetylated product = 86.5%,
 di-phenylthyl ether. = 12.5%
 other = 1%

EXAMPLE 11

Claisen Schmidt Condensation reaction

40mmol of acetophenone, 40 mmol of benzaldehyde and 1g of dodecane (Internal standard) was added to a round bottom flask and heated to 70°C. 0.5g of catalyst A, D, E or F was added and samples taken periodically for analysis by GC.



Acetophenone Benzaldehyde

A comparison of the conversions and selectivity obtained after 8 hour reaction is shown in **Table 4**

Catalyst	Conversion of Acetophenone %	Selectivity to chalcone %
A	30%	99%
E	44%	98%
F	33%	99%
D	5%	99%

Table 4

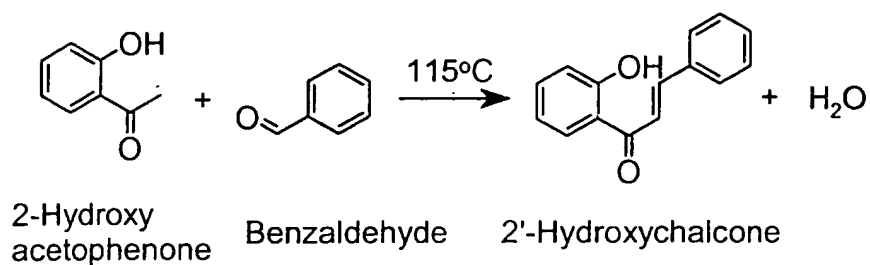
This activity of these catalysts increases with reaction temperature as illustrated in Table 5, after 24 hours using catalyst A

Reaction Temperature °C	Conversion of Acetophenone %
50	5
70	22
90	40
110	58
150	82

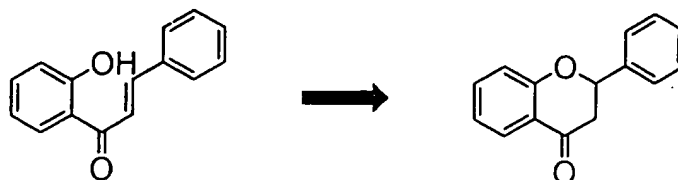
Table 5

EXAMPLE 12

Condensation Reaction



Further reaction to form the flavanone can also be observed.



40mmol of 2-hydroxyacetophenone, 40 mmol of benzaldehyde and 1g of dodecane (Internal standard) was added to a round bottom flask and heated to 150°C. 0.5g of catalyst A, was added and samples taken periodically for analysis by GC.

Under these conditions a 66% conversion of 2-hydroxyacetophenone was obtained with the following product selectivity's

hydroxychalcone = 65%

flavanone = 22%

other = 13%

CLAIMS:

1. A supported BF_3 catalyst system comprising a BF_3 /organic Brønsted base cocatalyst complex wherein BF_3 is attached directly to the surface of the support.
2. A supported BF_3 catalyst system according to Claim 1 in which the organic Brønsted base is an organic molecule containing oxygen, nitrogen or sulphur containing basic centres capable of being protonated to produce a material having a Pka value of +4 or lower.
3. A supported BF_3 catalyst system according to Claim 1 or Claim 2 in which the Brønsted base contains an oxygen containing basic centre.
4. A supported BF_3 catalyst system according to Claim 3 in which the Brønsted base is an alcohol, an ether, a ketone, an aldehyde, an ethoxyate or a carboxylic acid.
5. A supported BF_3 catalyst system occurring to any of the preceding claims in which the support is selected from silica, alumina and zirconia.
6. A supported catalyst system according to any of the preceding claims in which the support is mesoporous silica.
7. A supported catalyst system according to any of claims 1 to 5 in which the support is silica calcined at 500°C or above.
8. A process for the production of a catalyst system according to any of the preceding claims comprising mixing a solution of the BF_3 /organic Brønsted base cocatalyst complex with the support and removing excess solvent under conditions which does not remove the organic Brønsted base cocatalyst.
9. A process according to Claim 8 in which the excess solvent is removed under vacuum at a temperature below the boiling point of the organic Brønsted base cocatalyst.
10. A process according to Claim 8 or Claim 9 in which the solvent is a polar organic solvent which is capable of complexing with BF_3 .

11. A process according to Claim 10 in which the solvent is an oxy solvent.
12. A process according to Claim 11 in which the oxy solvent is an alcohol, an ester, a ketone, an aldehyde, an ethoxylate or a carboxylic acid.
13. The use of a catalyst system according to any of claims 1 to 7 in liquid phase reactions.
14. The use according to Claim 13 in which the reaction is selected from alkylation, polymerisation, etherification, esterification and condensation.

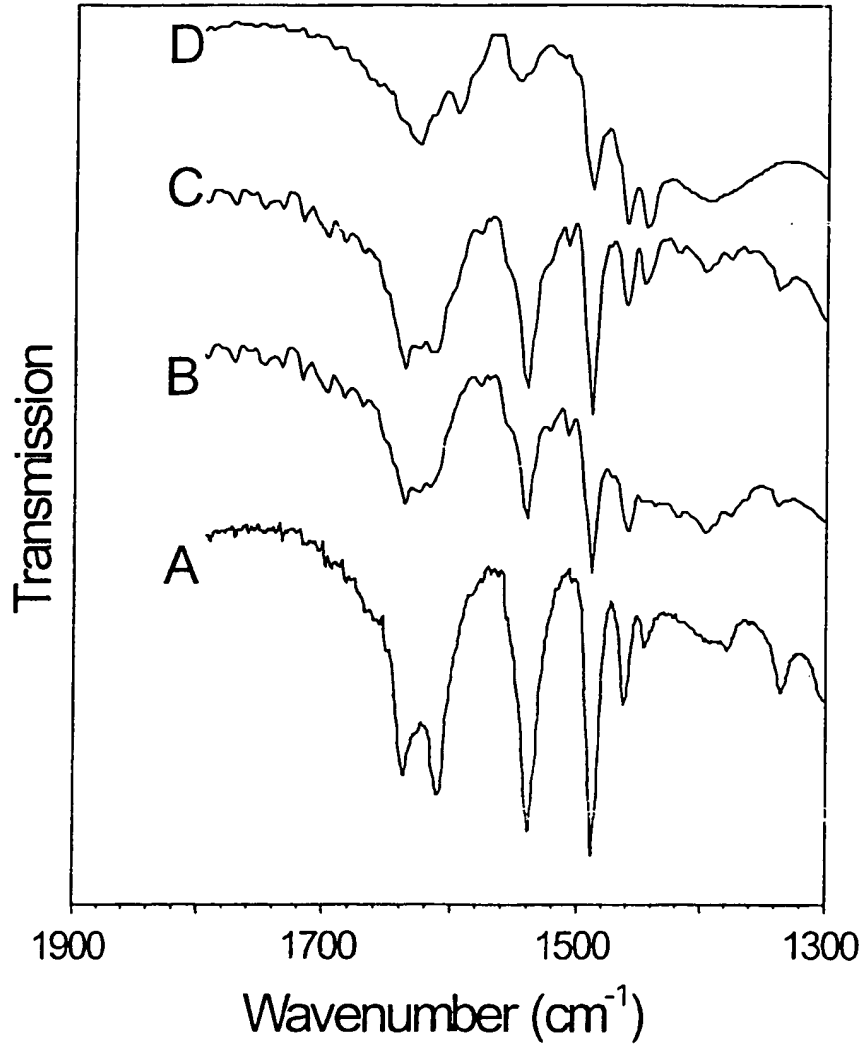


Fig. 1

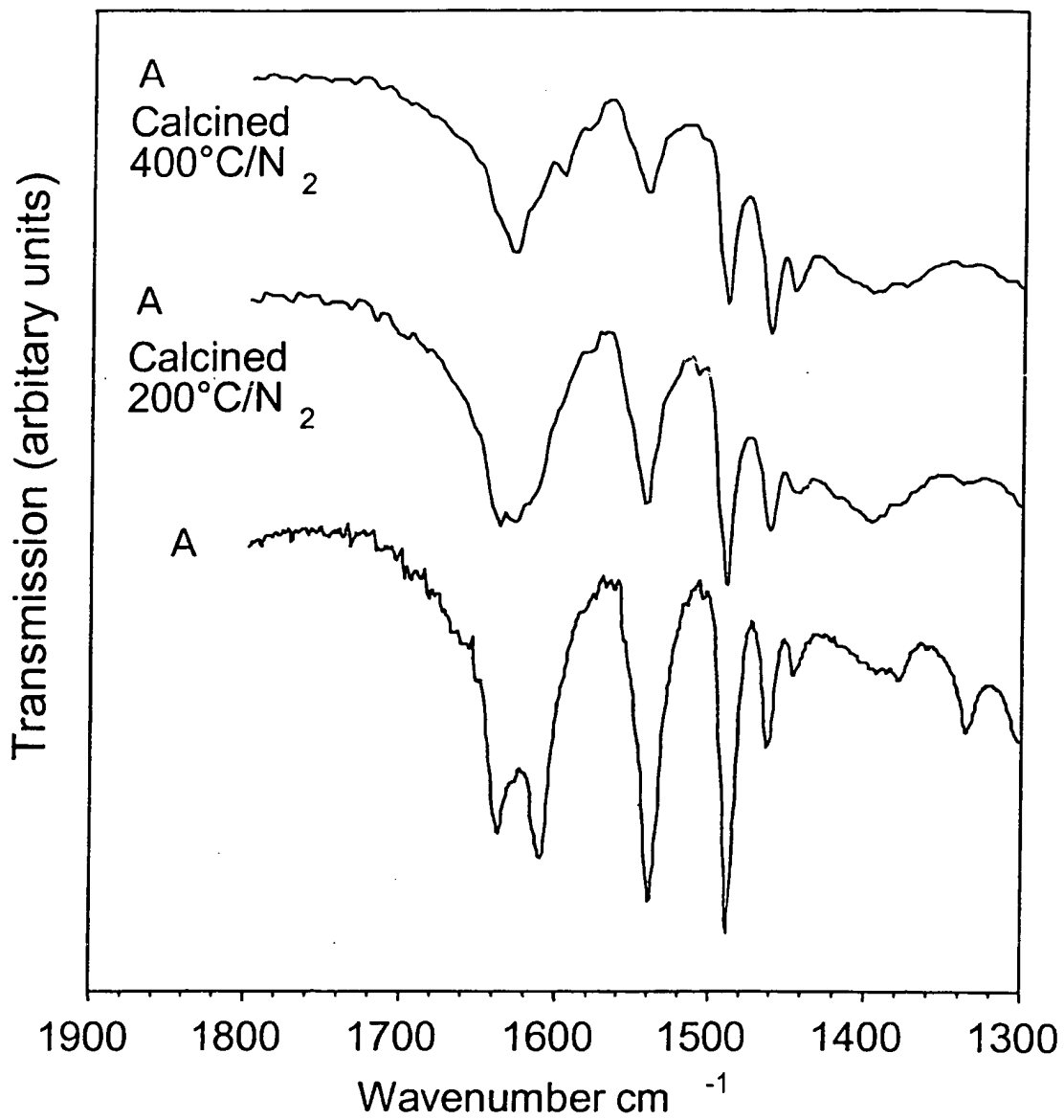


Fig. 2

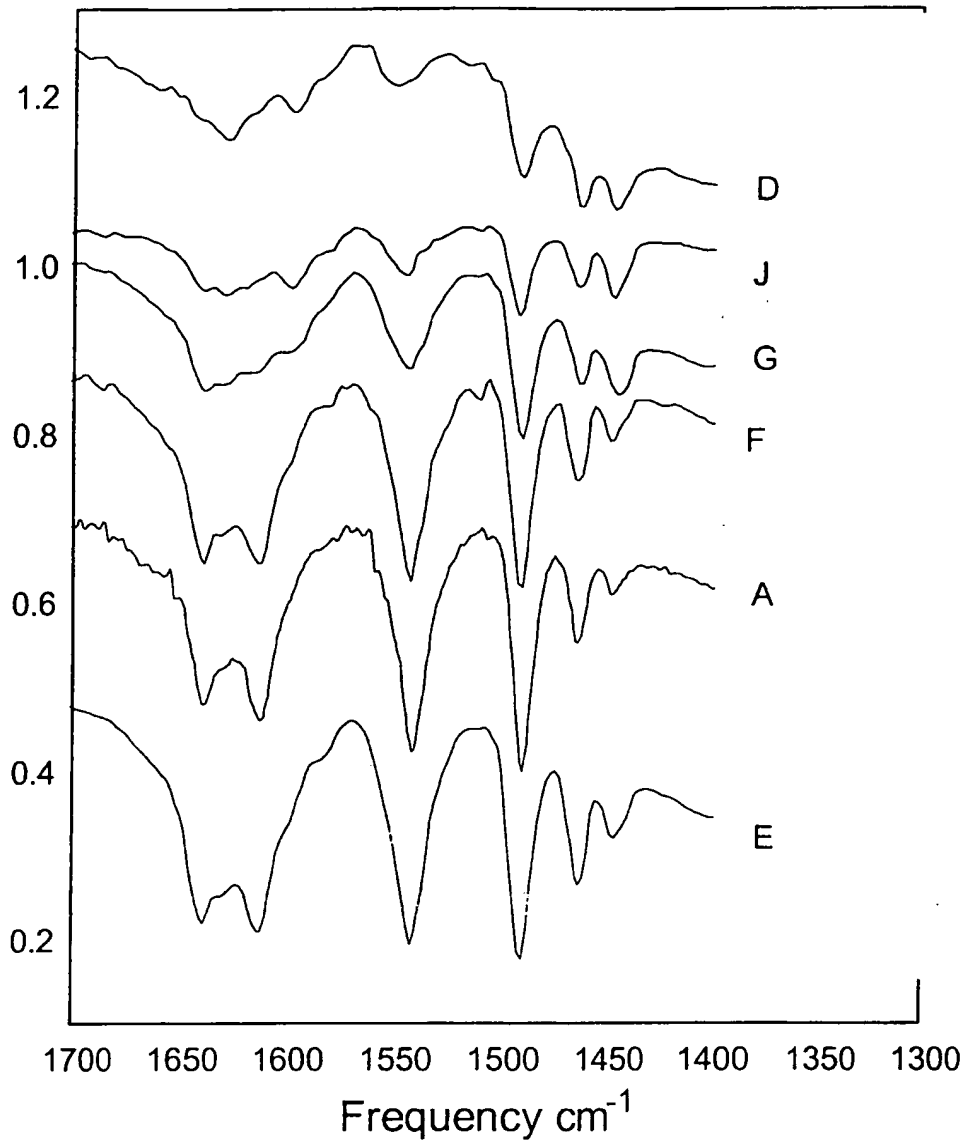


Fig. 3

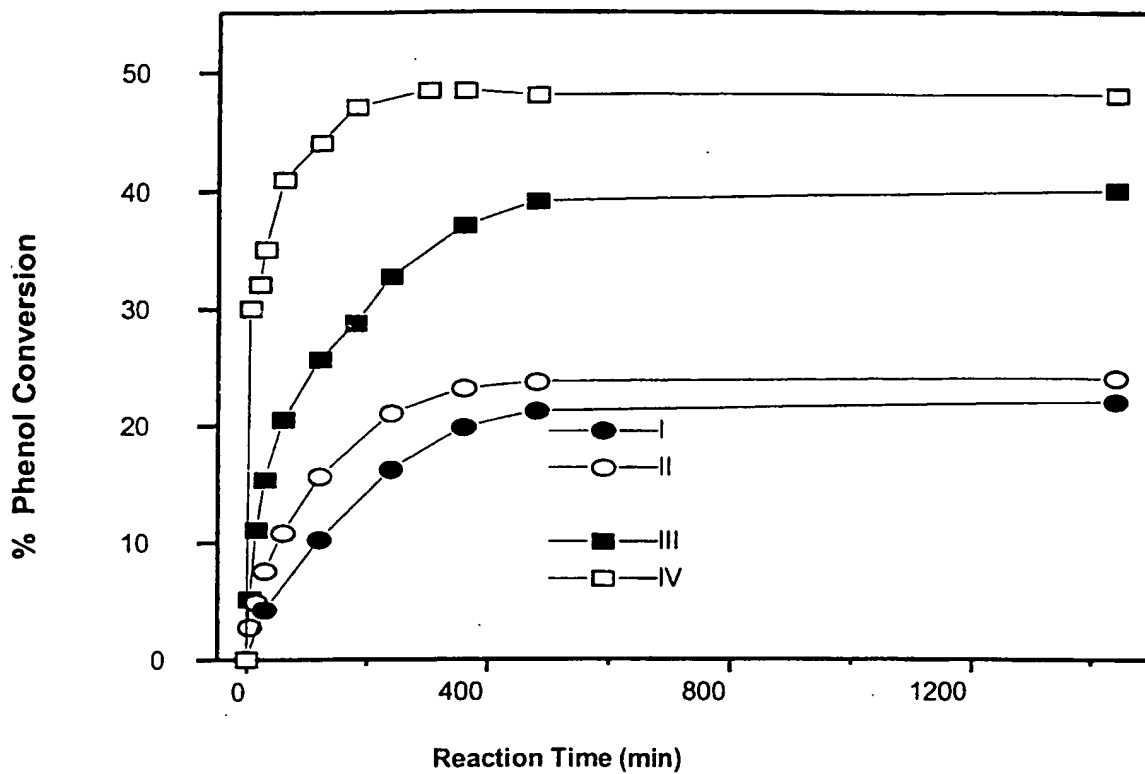


Fig. 4

5/9

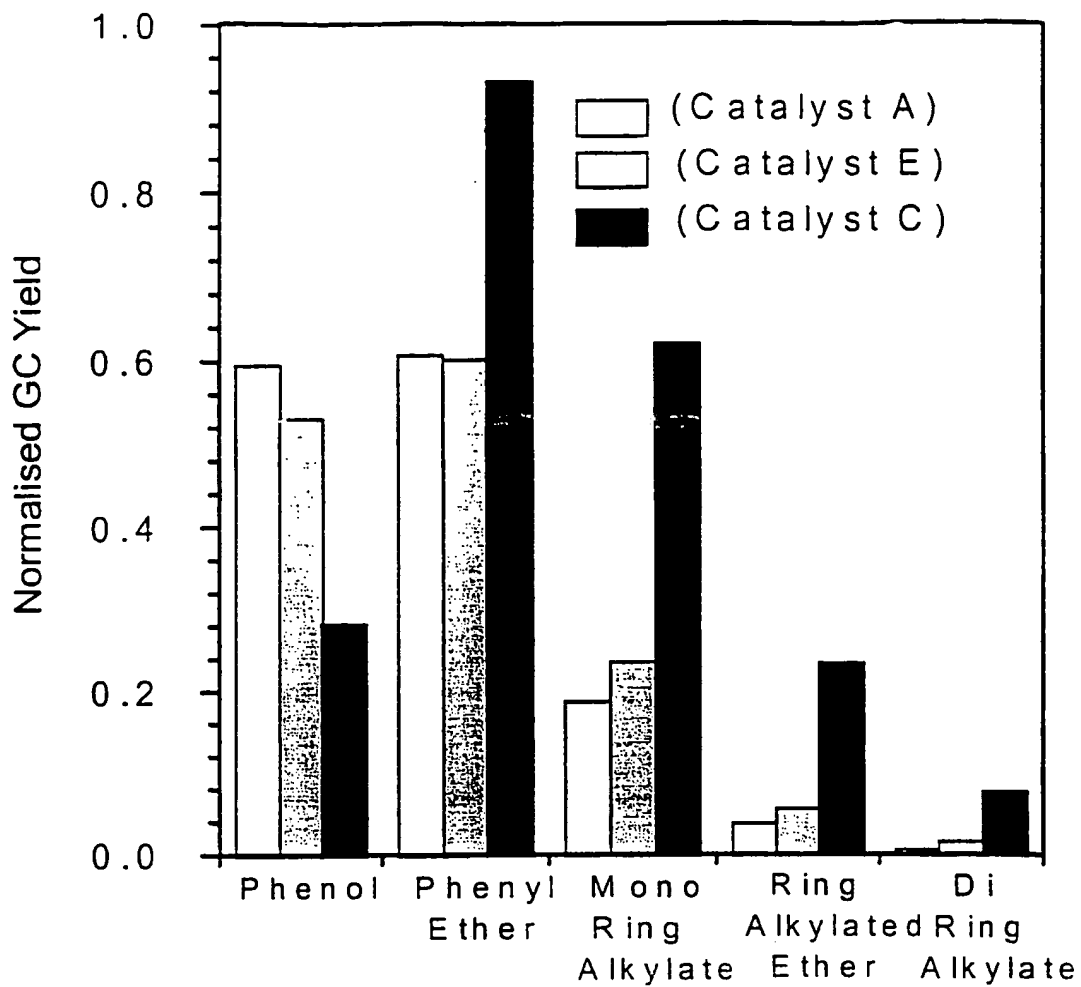


Fig. 5

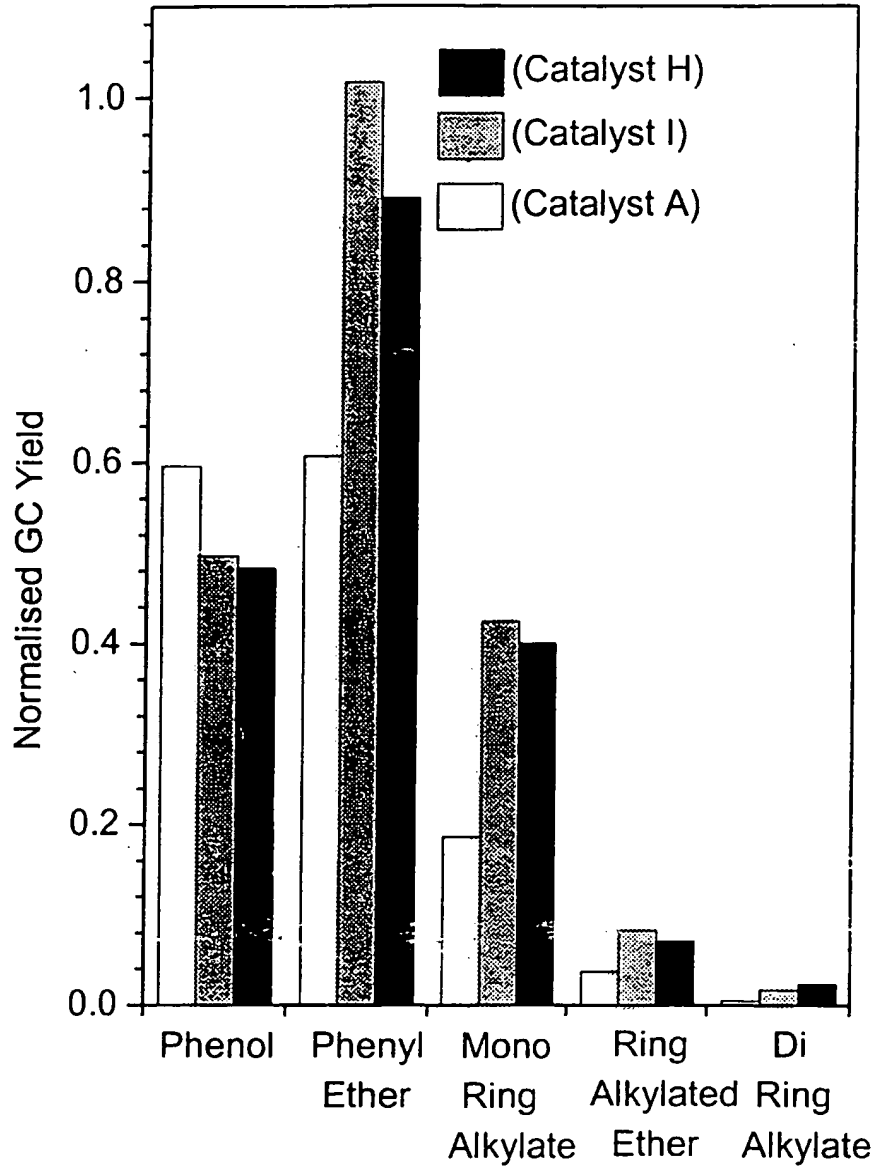


Fig. 6

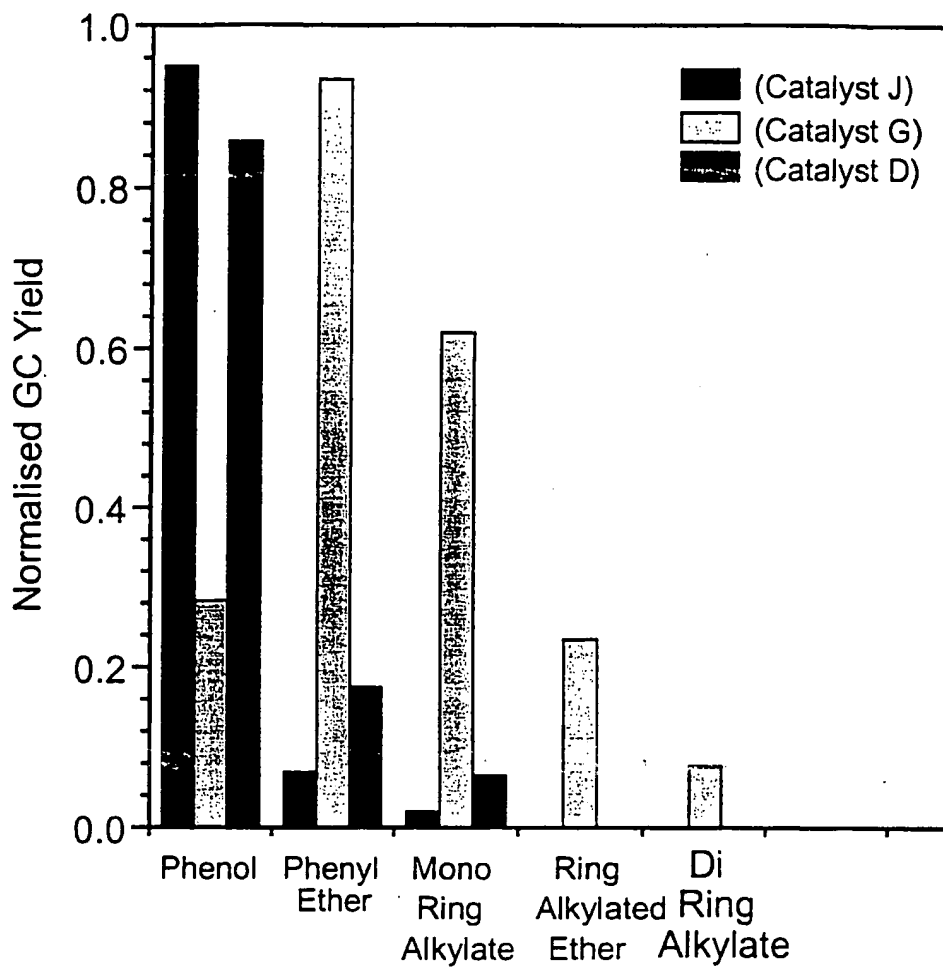
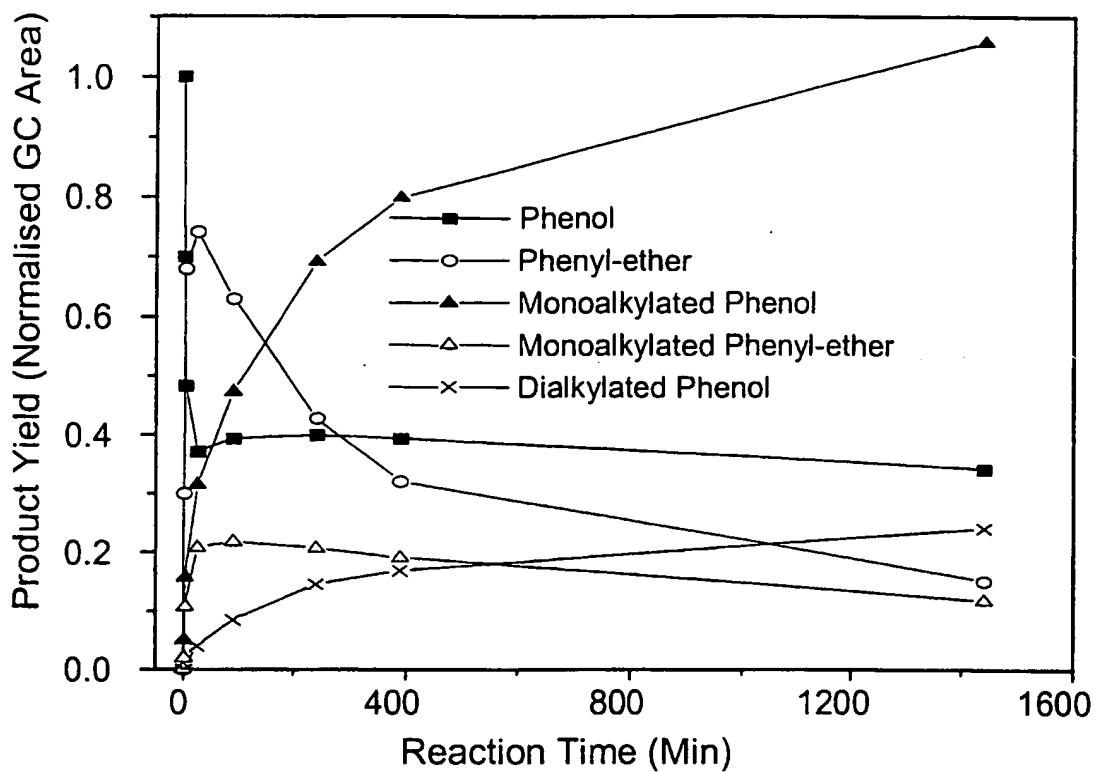


Fig. 7



**Fig. 8: Phenol Alkylation
Using Homogeneous BF_3**

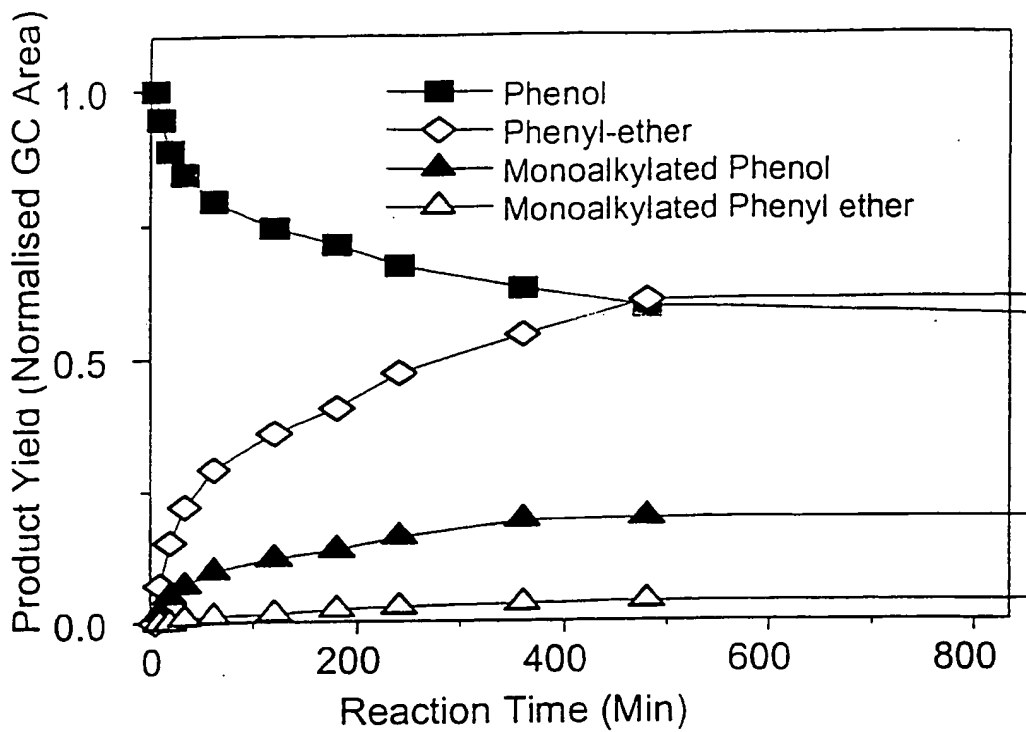


Fig. 9: Product distribution obtained using Heterogeneous BF_3/SiO_2 (Catalyst A)

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/EP 99/06528

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B01J27/12 B01J27/08				
According to International Patent Classification (IPC) or to both national classification and IPC				
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
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C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X Y A Y A A	US 3 525 699 A (KOPPEL PAUL M ET AL) 25 August 1970 (1970-08-25) claim 1 --- US 4 394 296 A (SWIFT HAROLD E ET AL) 19 July 1983 (1983-07-19) --- DE 14 93 285 A (UNIVERSAL OIL PRODUCTS) 3 April 1969 (1969-04-03) claim 1 --- WO 92 04977 A (CATALYTICA INC) 2 April 1992 (1992-04-02) --- EP 0 364 889 A (IDEMITSU PETROCHEMICAL CO) 25 April 1990 (1990-04-25) --- ---	1-5,8,10 14 14		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.				
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/06528

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 477 673 A (IDEMITSU PETROCHEMICAL CO) 1 April 1992 (1992-04-01) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/06528

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3525699 A	25-08-1970	NONE	
US 4394296 A	19-07-1983	US 4308414 A	29-12-1981
DE 1493285 A	03-04-1969	NL 135912 C NL 283749 A OA 528 A	15-07-1966
WO 9204977 A	02-04-1992	US 5171729 A US 5157197 A AT 150667 T AU 652190 B AU 8724191 A BR 9106886 A CN 1062307 A DE 69125384 D DE 69125384 T EP 0550640 A ES 2099169 T FI 931312 A JP 6504712 T MX 9101286 A NO 931120 A US 5365010 A US 5326923 A SK 25693 A CA 2092569 A	15-12-1992 20-10-1992 15-04-1997 18-08-1994 15-04-1992 27-09-1994 01-07-1992 30-04-1997 06-11-1997 14-07-1993 16-05-1997 24-05-1993 02-06-1994 04-05-1992 04-05-1992 15-11-1994 05-07-1994 06-10-1993 08-11-1992
EP 0364889 A	25-04-1990	JP 2001533 C JP 2108638 A JP 7017523 B JP 2275827 A US 4982042 A	20-12-1995 20-04-1990 01-03-1995 09-11-1990 01-01-1991
EP 0477673 A	01-04-1992	JP 2028654 C JP 4128242 A JP 7064757 B DE 69119011 D DE 69119011 T KR 146376 B US 5191140 A	19-03-1996 23-04-1992 12-07-1995 30-05-1996 12-09-1996 17-08-1998 02-03-1993

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁷ : B01J 27/12, 27/08</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/13792 (43) International Publication Date: 16 March 2000 (16.03.00)</p>
<p>(21) International Application Number: PCT/EP99/06528 (22) International Filing Date: 6 September 1999 (06.09.99) (30) Priority Data: 9819456.6 7 September 1998 (07.09.98) GB (71) Applicant: THE UNIVERSITY OF YORK [GB/GB]; Heslington Hall, Heslington, York YO10 5DD (GB). (72) Inventors: CLARK, James, H.; 15 Newlands Park Close, York YO10 3HW (GB). WILSON, Karen; 59 Kensington Street, Southbank, York YO23 1JA (GB). (74) Agent: BAWDEN, Peter, Charles; Bawden & Associates, 66A High Street, Harpenden, Hertfordshire AL5 2SP (GB).</p>	<p>(81) Designated States: ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i> <i>With amended claims.</i></p> <p>Date of publication of the amended claims: 2 June 2000 (02.06.00)</p>	
<p>(54) Title: SUPPORTED BF₃-COMPLEX SOLID ACID CATALYST, PREPARATION AND USE</p>		
<p>(57) Abstract</p> <p>A novel method to prepare solid acid catalysts by the reaction of liquid BF₃ precursors with inorganic oxide supports is reported. The resulting solid acid catalyst exhibits strong Brønsted acidity that can be tuned by appropriate selection of cocatalyst, solvent or calcination temperature, and can be used to catalyse organic reactions.</p>		

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AMENDED CLAIMS

[received by the International Bureau on 6 April 2000 (06.04.00)]

original claims 1, 2, 5, and 8 amended;

new claims 15-21 added; remaining claims unchanged (3 pages)]

1. A supported BF₃ catalyst system comprising a BF₃/organic Brønsted base cocatalyst complex wherein BF₃ is attached directly to the surface of the support and the support is not alumina.
2. A supported BF₃ catalyst system according to Claim 1 in which the organic Brønsted base is an organic molecule containing oxygen, nitrogen or sulphur containing basic centres capable of being protonated to produce a material having a pK_a value of +4 or lower.
3. A supported BF₃ catalyst system according to Claim 1 or Claim 2 in which the Brønsted base contains an oxygen containing a basic centre.
4. A supported BF₃ catalyst system according to Claim 3 in which the Brønsted base is an alcohol, an ether, a ketone, an aldehyde, an ethoxylate or a carboxylic acid.
5. A supported BF₃ catalyst system according to any of the preceding claims in which the support is selected from silica and zirconia.
6. A supported catalyst system according to any of the preceding claims in which the support is mesoporous silica.
7. A supported catalyst according to any of Claims 1 to 5 in which the support is silica calcined at 500°C or above.
8. A process for the production of a catalyst system comprising mixing a solution of the BF₃/organic Brønsted base cocatalyst complex with a support and removing excess solvent under conditions which do not remove the organic Brønsted base cocatalyst.

9. A process according to Claim 8 in which the excess solvent is removed under vacuum at a temperature below the boiling point of the organic Brønsted base cocatalyst.
10. A process according to Claim 8 or Claim 9 in which the solvent is a polar organic solvent which is capable of complexing with BF₃.
11. A process according to Claim 10 in which the solvent is an oxy solvent.
12. A process according to Claim 11 in which the oxy solvent is an alcohol, an ester, a ketone, an aldehyde, an ethoxylate or a carboxylic acid.
13. The use of a catalyst system according to any of Claims 1 to 7 in liquid phase reactions.
14. The use according to Claim 13 in which the reaction is selected from alkylation, polymerisation, etherification, esterification and condensation.
15. A catalysed reaction in which the catalyst is a supported BF₃ catalyst system comprising a BF₃/organic Brønsted base cocatalyst complex wherein BF₃ is attached directly to the surface of the support, reactions which are performed in the gaseous phase and in which the catalyst is BF₃ supported on alumina in the presence of methanol being excluded.
16. A catalysed reaction in which the catalyst is a supported BF₃ catalyst system comprising a BF₃/organic Brønsted base cocatalyst complex, wherein BF₃ is attached directly to the surface of the support.
17. A catalysed reaction according to Claim 15 or Claim 16 which is a liquid phase reaction.
18. A catalysed reaction according to any of Claims 15 to 17, in which the reaction is selected from alkylation, polymerisation, etherification and condensation.

19. A catalysed reaction according to any of Claims 15 to 18 in which the support is selected from silica, alumina or zirconia.
20. A catalysed reaction according to any of Claims 15 to 19, in which the organic Brønsted base is an organic molecule containing oxygen, nitrogen or sulphur containing basic centres capable of being protonated to produce a material having a pKa value of +4 or lower.
21. A catalysed reaction according to Claim 20 in which the Brønsted base is an alcohol, an ether, a ketone, an aldehyde, an ethoxylate or a carboxylic acid.